# Possible room temperature superconductivity in conductors obtained by bringing alkanes into contact with a graphite surface

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Electrical resistances of conductors obtained by bringing alkanes into contact with a graphite surface have been investigated at room temperatures. Ring current in a ring-shaped container into which n-octane-soaked thin graphite flakes were compressed did not decay for 50 days at room temperature. After two HOPG plates were immersed into n-heptane and n-octane at room temperature, changes in resistances of the two samples were measured by four terminal technique. The measurement showed that the resistances of these samples decrease to less than the smallest resistance that can be measured with a high resolution digital voltmeter ($0.1\mu$V). The observation of persistent currents in the ring-shaped container suggests that the HOPG plates immersed in n-heptane and n-octane really entered zero-resistance state at room temperature. These results suggest that room temperature superconductor may be obtained by bringing alkanes into contact with a graphite surface.  [http://dx.doi.org/10.1063/1.4808207]

In 1986 Bednorz and Müller discovered that the material $La_{2-x}Ba_xCuO_4$ becomes superconducting with a $T_c$ which is maximum at 38 K for x = 0.15.[1] Within a matter of months the related compound $YBa_2Cu_3O_7$ was discovered to have $T_c$ = 92 K which can operate in liquid nitrogen.[2] However, although a large number of researchers engaged in study of the related compounds, the highest confirmed value of $T_c$ remains at 135 K under atmospheric pressure.[3] Although a number of researchers have tried to seek for a room-temperature superconductor until now,[4,5] it has not been discovered yet.

Kopelevich *et al.* reported ferromagnetic and superconducting-like magnetization hysteresis loops in some HOPG samples below and above room temperature suggesting the local superconductivity in graphite in 2000.[6,7] But the origins of the observations that were explained by local superconductivity are still unclear. A considerable amount of studies had reported superconductivity in intercalated graphite compounds or doped graphite.[8–11] Recently, Scheike *et al.* reported that flakes of graphite soaked in pure water show clear and reproducible granular superconducting at temperatures of greater than 100 °C.[12] But the researchers have not been able to show that superconducting current passes through the water treated graphite grains.

In the process of studying a reactivity of graphite surface, we thought that if graphite surface and alkanes (normal saturated hydrocarbons) are brought into contact with each other, a proton moving freely on the graphite surface without activation energy could be produced and this proton might cause superconductivity at room temperature and above.[13–15] Then we have tried to compress graphite thin flakes and n-octane into a polytetrafluoroethylene (PTFE) ring-shaped container and have produced induction ring current in the ring-shaped container. We have investigated whether this ring current persists with no decay at room temperature or not. Furthermore, in order to observe that a conductor comprising graphite plate and alkanes enters superconducting state at room temperature, we have measured the change in resistance of the conductor after the graphite plate is immersed in

 

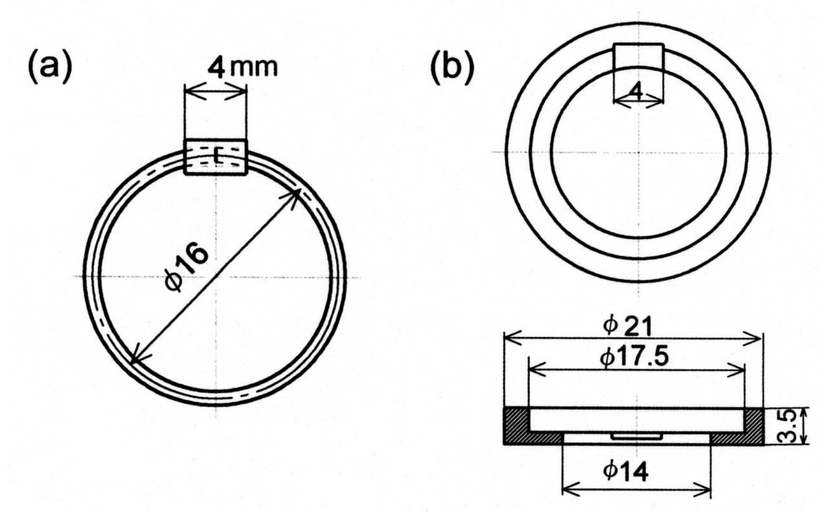


FIG. 1. (a) A top view schematically illustrating a PTFE ring-shaped container. (b) Top and cross-sectional views schematically illustrating a PTFE holding jig.

alkanes. In this report, we discuss room temperature superconductivity in the conductors comprising graphite surface and alkanes on the basis of these experimental results.

In order to obtain evidence that the conductor really conducts electricity with zero resistance, we carried out following experiments. Thin graphite flakes obtained from highly oriented pyrolytic graphite (HOPG) (Momentive Performance Materials Inc., Grade: ZYA) were compressed into a PTFE tube (inner diameter: 0.9 mm, outer diameter: 1.5 mm, length: ∼50 mm) in random orientation. The graphite flakes had an average thickness of ∼0.01mm and an average diameter of ∼1 mm. The PTFE tube was soaked in n-octane for one day. Then we made a closed loop of the tube, which has a ring diameter of 16 mm (see Fig. 1(a)). Both ends of the tube, which were brought into contact with each other, were fixed by a glass tube (inner diameter: 1.6 mm, outer diameter: 2.5 mm, length: 4 mm). The PTFE ring-shaped container made in such a way was mounted in a PTFE holding jig (see Fig. 1(b)) so that both ends do not separate. The total weights of thin graphite flakes and n-octane compressed into the ring-shaped container were 0.0344 and 0.0148 g, respectively. The contact point of thin graphite flakes compressed into the ring-shaped container was confirmed by microscope.

In order to confirm whether a ring current in the ring-shaped container persists or not, a magnetization and measurement system was made. Figure 2 illustrates the magnetization and measurement system. Figure 2(a) is a front view illustrating an arm portion placed in the magnetization position. Figure 2(b) illustrates a magnetization and measurement unit. Figure 2(c) is a top view illustrating the arm portion rotated to be out of a magnetization position. A fixing jig made of acrylic resin is fitted into a fixing hole provided near one end of the acrylic resin base. A recess is provided on top of the fixing jig such that a hall probe holder made of PTFE is received in the recess and the ring-shaped container placed in the holding jig is put in the recess. The fixing jig and the hall probe holder each include a vertically extending through-hole such that the hall probe is received in this through-hole concentrically with the ring-shaped container. The through-hole of the hall probe holder is made such that the hall probe can be slid and moved in a vertical direction and held at any position. An X-Z direction positioning stage made of aluminum stands on the acrylic resin base near the other end of the base. The plate-shaped arm portion made of acrylic resin is provided at a top end of the X-Z direction positioning stage via a plastic screw and a cylindrical body made of PTFE. The arm portion is held by a plastic screw and rotatable thereabout, the plastic screw being an axis of rotation. The arm portion is parallel to the base.

An induction coil (number of turns being 50) is held by a round bar made of acrylic resin and a plastic screw such that the induction coil resides immediately above the ring-shaped container and concentrically with the ring-shaped container when the arm portion is rotated and placed in the

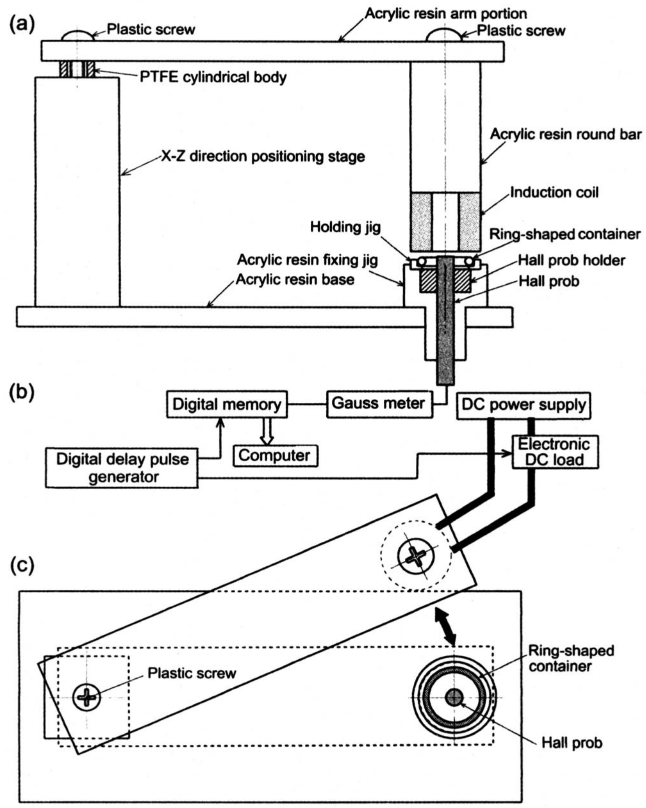


FIG. 2. (a) A front view of the magnetization and measurement system. (b) The magnetization and measurement unit. (c) A top view schematically illustrating the magnetization and measurement system.

magnetization position (indicated by dashed lines in Fig. 2(c)). This induction coil is adapted to produce induction ring current for the sample within the ring-shaped container so that the magnetic field is generated in the axial direction of the induction coil. A direct-current power source is connected via the electronic DC load device to the induction coil. A digital delayed-pulse generator (Stanford Research Systems, Inc., DG535) is connected to the electronic DC load device for driving the electronic DC load device to control turning on and off of the induction coil.

When an electric current of about 7 A flowed in the induction coil, a magnetic field of 50 G was detected by the hall probe. If an energizing period of the induction coil was approximately 15 seconds, a signal was transmitted by the digital delayed-pulse generator to the electronic DC load device to stop energization of the coil rapidly. After that, in order to avoid inconvenience that may undermine the accuracy of measurement, such as Joule heat that is produced in the induction coil and transferred to the sensor close to the head of the hall probe, the arm portion was immediately rotated after stoppage of energization and thus the induction coil was detached from the hall probe.

The hall probe is connected to a gaussmeter provided in the magnetization and measurement unit (Lake Shore Cryotronics, Inc.: Model 455; Hall probe: HMNA1904VR). The magnetic field due to the sample contained within the ring-shaped container is detected by the hall probe and the gaussmeter and stored in the digital memory unit.

After the current through the induction coil (7 A) was shut off using the DC electronic load device, a magnetic field from the ring-shaped container continued to be detected for one hour at room temperature. The PTFE jig holding the ring-shaped container was rapidly removed from the recess of the fixing jig fitted in the base. Figure 3(a) shows changes in magnetic field measured by the hall sensor when the PTFE jig holding the ring-shaped container was rapidly removed from the recess of the fixing jig. It is seen from Fig. 3(a) that the magnetic field that had been continuously detected was produced by the sample comprising the graphite and the n-octane within the container.

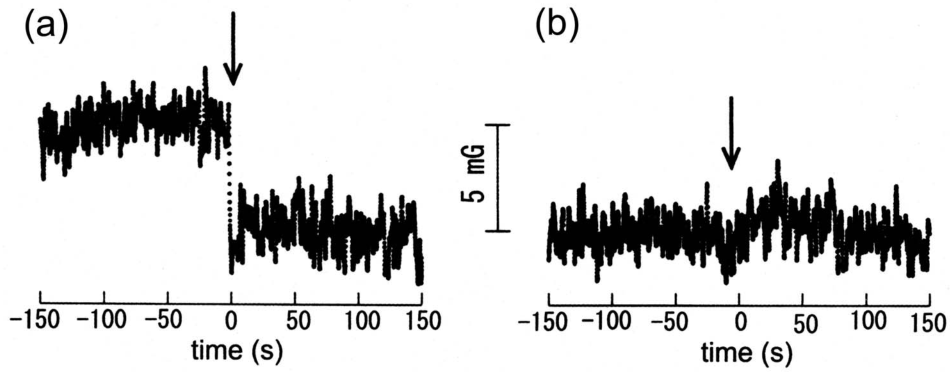


FIG. 3. (a) Changes in the magnetic field detected when the ring-shaped container was rapidly removed from the magnetization and measurement system. (b) Changes in the magnetic field when the ring-shaped container that had been disconnected and had been again placed in the magnetization and measurement system was rapidly removed from the magnetization and measurement system. In (a) and (b), an arrow indicates a timing for removing the ring-shaped container from the system.

The direction of the magnetic field due to the ring-shaped container was the same as the direction of the applied magnetic field produced by the induction coil. Since the magnetic field is induced by rapid decrease in the applied magnetic field, the direction of the magnetic field due to the ring-shaped container measured by the hall sensor is consistent with Farady's law of electromagnetic induction. After that (three minutes later), the ring-shaped container was temporarily disconnected and then connected again. It was again confirmed by microscope that both ends of the sample compressed into the PTFE tube were connected. The PTFE jig holding the ring-shaped container was again placed in the recess of the fixing jig. However, no change in magnetic field was detected by the hall sensor when the PTFE jig holding the container was rapidly removed from the recess of the fixing jig (see Fig. 3(b)). Thus it is seen from Figs. 3(a) and 3(b) that the ring-shaped sample that had once been separated lost the magnetic field. In the two experiments, the same holding jig was used. Since the magnetization system is made up of non-magnetic materials, there is little likelihood that magnetic impurities adhere to the PTFE ring-shaped container and the PTFE holding jig. If magnetic impurities in the sample within the ring-shaped container or on the surface of the holding jig are responsible for the magnetic field detected for the first sample by the hall sensor, change in magnetic field should also be detected for the ring-shaped container that had once been disconnected when it was rapidly removed from the system. Therefore, it can be concluded that the magnetic field measured for the first sample within the ring-shaped container is due to ring current, not to magnetic impurities. Thus it is confirmed that current in the ring-shaped container persisted for one hour or more after the current through the coil was shut off and the magnetic field was created by the rotational current in the ring-shaped container.

Ring current in the ring-shaped container into which n-octane soaked thin graphite flakes were compressed was again produced by the magnetization system. The ring-shaped container was kept in an ordinary jam jar with a screw top (capacity: $\sim$50 ml) together with n-octane ($\sim$1ml) at room temperature for 50 days. The magnetic field distribution in central axial direction of the ring-shaped container was measured with hall probe using a micrometer in double walled container made of permalloy. Figure 4 shows the central axial magnetic field distributions of the ring-shaped container 24 days and 50 days after the current through the induction coil was shut off. The magnetic field distribution after 50-days storage agrees with the magnetic field distribution after 24-days storage (this distribution also agrees with the magnetic field distribution immediately after the current through the induction coil was shut off), which shows that the ring current produced in the conductor comprising the graphite and the n-octane did not diminish but was continuously maintained. In Fig. 4, the solid line represents a calculated value of the magnetic field distribution in the central axial direction due to ring current through a ring-shape coil that has the same dimensions as the ring-shaped container. Since the actual magnetic field distribution faithfully agrees with the calculated

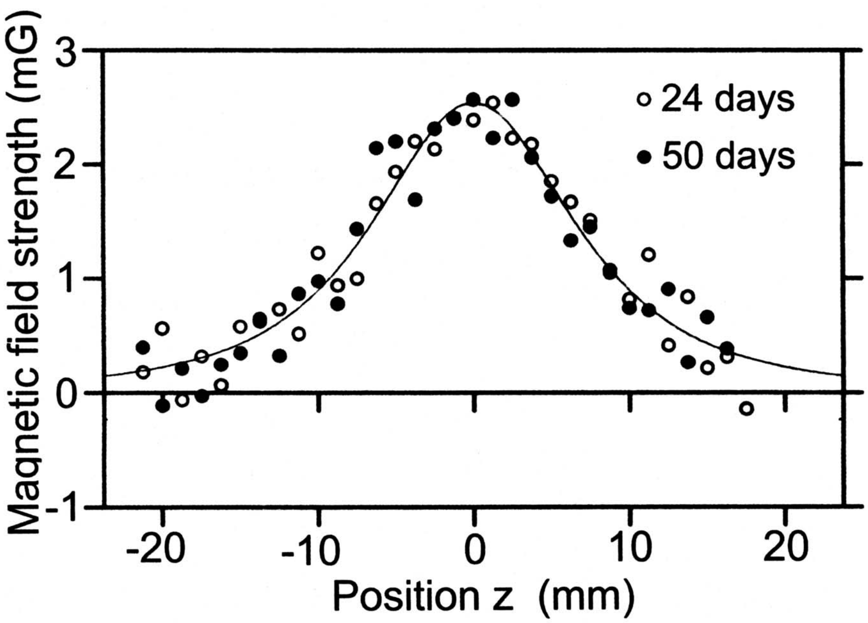


FIG. 4. Magnetic field distributions along an axial direction of the ring-shaped container 24 days and 50 days after the current through the coil was shut off. The solid line represents a calculated value of the magnetic field distribution in the central axial direction due to ring current through a ring-shape coil that has the same dimensions as the ring-shaped container.

magnetic field distribution due to the ring current, it was verified that the actual magnetic field was due to the ring current, not to magnetic impurities.

Electrical resistances of the conductors comprising HOPG plate and alkanes were measured by the standard four terminal technique with an AC of frequency of 1 kHz. An HOPG plate was fixed on a PTFE plate of 0.5 mm in thickness by using double-sided adhesive tapes. Four leads connected to the sample were used. The first pair of leads was connected to an AC current source. The second pair of leads was connected to AC voltage measuring instrument. An 100-Ω resistor was connected in series with the AC current source. The four leads were fixed to four alligator clips with solder. The HOPG plate and the PTFE plate were held with the four alligator clips.

The sample for resistance measurement was put in a laboratory dish. After it was confirmed that the resistivity of HOPG ($4 \times 10^{-5}$ Ωcm)[16] was accurately measured, the HOPG plate was immersed in alkane by pouring alkane into the laboratory dish. The accurate resistivity measurement of HOPG provides confirmation that there are no problems with the resistance measurement.

Figures 5(a) and 5(b) shows changes in resistance of the samples after two HOPG plates were immersed into n-heptane and n-octane at room temperature, respectively. The resistivity was calculated from a measured resistance, a width and a thickness of the HOPG plate, and a distance between two contacts for measuring a voltage. In Figs. 5, a broken line indicates the resistivity of HOPG ($4 \times 10^{-5}$ Ωcm).[16] Figure 5(a) shows that the resistance of the sample suddenly dropped to zero ∼160 s after the HOPG plate was immersed in n-heptane. Figure 5(b) shows that the resistance of the sample suddenly dropped to zero ∼270 s after the HOPG plate was immersed in n-octane. Taking the results obtained for the compressed n-octane soaked graphite flakes into account, it can be concluded that the conductors entered zero-resistance state at room temperature.

The resolution of the voltmeter used for measuring the resistance of sample is 0.1 $\mu$V. Figure 5(a) shows changes in resistance of the sample measured with a current of 100 mA after the HOPG sample were immersed in n-heptane. In this case, the minimum resistance that can be measured by the voltmeter is $1 \times 10^{-6}$ Ω. If the resistance of the sample becomes a value smaller than $1 \times 10^{-6}$ Ω, that is, the output voltage of the voltmeter becomes zero, we decide that the sample enters the zero-resistance state. Figure 5(a) shows that the resistance of the sample changed to a value smaller than $1 \times 10^{-6}$ Ω from 0.00028 Ω, indicating that the resistance decreased more

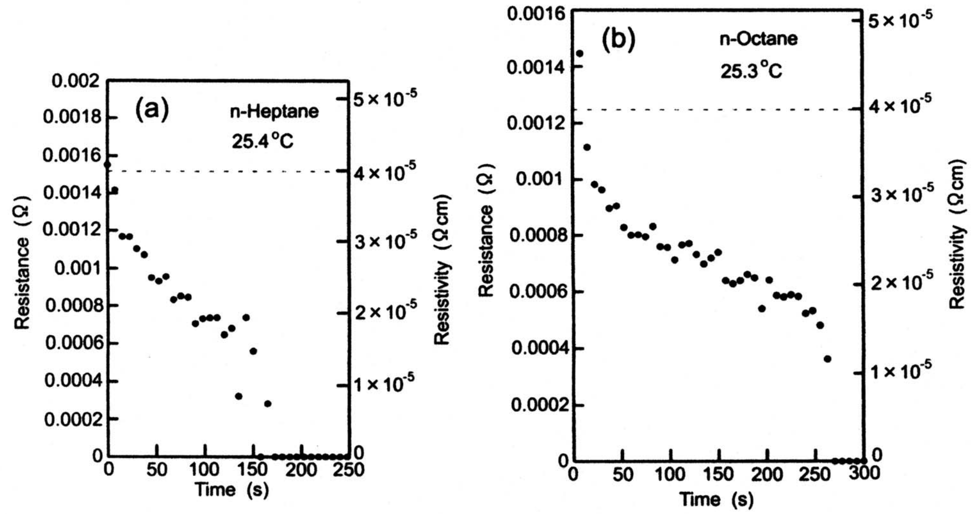


FIG. 5. Changes in resistance after HOPG samples were immersed in alkanes (n-heptane and n-octane). In the case of n-heptane, a HOPG plate (0.3 cm width × 0.07 cm thickness) was used and the distance between two contacts for measuring a voltage was 0.8 cm. The resistance was measured with 100 mA. In the case of n-octane, a HOPG plate (0.4 cm width × 0.04 cm thickness) was used and the distance between two contacts was 0.5 cm. The resistance was measured with 110 mA.

than two orders of magnitude in 7.5 s. A time constant of coil is obtained by L/R, where R is a resistance of coil electric wire and L is a self-inductance of coil. The self-inductance L is obtained by the equation $L = \mu_0 a\{\mathrm{In}(8a/\rho) - 1.75\}$, where a is a radius of coil, $\rho$ is a radius of coil wire, $\mu_0$ is the magnetic permeability of vacuum ($4\pi \times 10^{-7}$ H/m). In the experiments mentioned above, the radius of coil and the inside diameter of PTFE tube are 0.8 cm and 0.96 mm, respectively. By substituting $a = 0.8$ cm and $\rho = 0.048$ cm into the above equation, the self-inductance of the coil is calculated to be $3.16 \times 10^{-8}$ H. If the resistance of the coil is assumed to be $1 \times 10^{-6}$ Ω, the time constant of the coil is $3.16 \times 10^{-2}$ s. After passing electric current through the coil, the current is given by the equation $I(t) = I_0 \exp(-Rt/L)$. Here, $I_0$ is an initial current and t is time. When the resistance of the coil wire is $1 \times 10^{-6}$ Ω, the initial current becomes smaller than $1/10^{13}$ in 1 s. If we assume that the initial current decreases to 99% in 50 days, the resistance of coil wire is smaller than $7.36 \times 10^{-17}$ Ω. It is inferred from the calculation that after the resistance of the conductor reached the minimum measurable resistance ($1 \times 10^{-6}$ Ω), it decreased rapidly and got closer and closer to zero.

It has recently been demonstrated that in HOPG samples, regions with "metaliclike" and "insulatinglike" behaviors coexist and the internal structure of bulk HOPG samples is not homogeneous in the micrometer range.[17] This find suggests that HOPG samples may have to be considered as composite materials. In carbon-composite materials, apparent negative resistance has been measured by four terminal technique, which has been explained by the backflow of electrons in the unexpected direction relative to the applied voltage gradient.[18] If current paths responsible for apparent negative resistance are combined with current paths that causes normal resistance, there is a possibility that zero apparent resistance may be measured by four terminal technique. However, the current paths in the HOPG sample immersed in alkanes will not change because there is almost no pressure exerted upon the HOPG samples and its temperature did not change during the resistance measurement. Therefore, zero resistance state observed for the HOPG samples immersed in alkanes is not due to changes of current paths that can occur in composite materials. It is considered almost certain that the HOPG sample immersed in alkanes (n-heptane and n-octane) really entered zero-resistance state.

In summary, we have demonstrated that the bulk material made by compressing thin graphite flakes and n-octane into the PTFE tube can conduct electricity with zero resistance at room temperature. Resistance measurements using four terminal technique show that after the HOPG plate was immersed in alkanes (n-heptane and n-octane) at room temperature, the resistance of the HOPG plate decreased to zero and the zero-resistance state persisted. The measurement of persistent currents in the ring-shaped container into which n-octane-soaked thin graphite flakes were compressed suggests that the conductor comprising HOPG plate and n-octane or n-heptane may really enter zero resistance state at room temperature. It can be concluded that room temperature superconductor might be obtained by bringing alkanes into contact with graphite surface.


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